

Micro-Constitutive Model Study of PMN-0.32PT Relaxor Ferroelectric Single Crystal

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Abstract

In present paper, stress-strain relationship of $\langle 001 \rangle$ oriented PMN-0.32PT relaxor ferroelectric single crystals has been investigated. Polarization rotation model is developed to explain the observed behaviors of PMN-0.32PT. Stress-strain curve of ferroelectric single crystal BaTiO₃ is calculated with the first principle method. Results show that the polarization rotation model is reasonable. Based on the polarization rotation model, a micromechanical constitutive model of PMN-0.32PT is constructed. It is shown that the developed model can faithfully capture the typical characteristic of the observed behavior of $\langle 001 \rangle$ oriented PMN-0.32PT.

Keywords

Ferroelectric Single Crystal; Polarization Rotation; Micromechanical Model; First Principle Method

Introduction

Note that PZN-PT and PMN-PT single crystals usually experience electric and/or mechanical loading during their in-service life. It has been shown that externally applied loading has significant effect on the properties of these crystals[1]. It has been shown loading in the form of electric field[1-3], and stress[4], can lead to polarization switching and phase transition, which changes dramatically alter their electromechanical properties. A mature level understanding of their responses to electrical, mechanical and temperature loading condition is thus essential to fulfill the applications of these crystals. A number of studies have focused on experiment, but the constitutive model of ferroelectric single is absent. Huber[5] and Bhattacharya[6-7] et.al established a model based on the micromechanical method, but the simulation can not describe experimental result well.

In this study, a polarization rotation model will be suggested to explain the stress-strain response of PMN-0.32PT. In order to validate that model, the stress-strain curve along $\langle 001 \rangle$ crystallographic direction of ferroelectric single crystals BaTiO₃ has been simulated in first principle method. Finally, based on the polarization rotation model, a

constitutive model based on micromechanical method is constructed .

Experimental Results and Discussion

Experimental setup is shown in Fig. 1 to allow simultaneously imposing uniaxial stress and electric field to the specimen along the thickness direction. Mechanical load is applied by a servo-hydraulic materials test system (MTS). During test, the compressive stress loading and unloading cycles being $-0.4 \rightarrow -12 \rightarrow -0.4$ MPa, $-0.4 \rightarrow -40 \rightarrow -0.4$ MPa, and $-0.4 \rightarrow -60 \rightarrow -0.4$ MPa, respectively. After each stress cycle, a unipolar electric field in the form of triangle wave with magnitude of 0.5kV/mm and frequency of 0.02Hz is applied to the specimen to ensure the specimen return to its initial state.

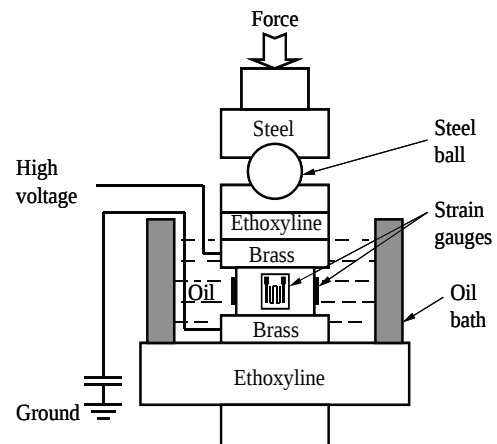


FIG.1 THE SKETCH of EXPERIMENTAL SET

Measured $\sigma_{33} - \epsilon_{33}$ responses of $\langle 001 \rangle$ -oriented PMN-0.32PT single crystal under the compressive stress loading and unloading cycles with the maximum magnitudes being 12MPa, 40MPa and 60MPa, respectively, are shown in Fig. 2. For the 40MPa and 60MPa stress cycles (Fig. 2), the stress induced behavior of PMN-0.32PT single crystals shows shape memory feature. This can be explained by the polarization vector rotation mechanism. The detail description of polarization vector rotation model can refer to our paper [8].

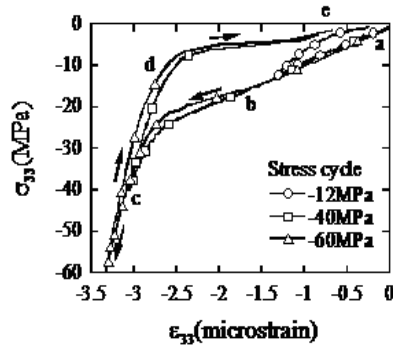


FIG.2 STRESS-STRAIN CURVES OF UNDER THE LOADING OF 12 MPa,40MPa,60MPa

First Principle Calculation of Stress-Strain

Calculation Methodology

PMN-PT and BaTiO₃ have the similar ABO₃ structure, so they have the similar ferroelectric properties. There is only Ti⁴⁺ particle in B site of BaTiO₃, however, there is not only Ti⁴⁺ but also minin Mn⁴⁺ and Ni²⁺ particle in B site of PMN-PT. So the single cell of BaTiO₃ is convenient in calculation and it keeps the similar ferroelectric to PMN-PT.

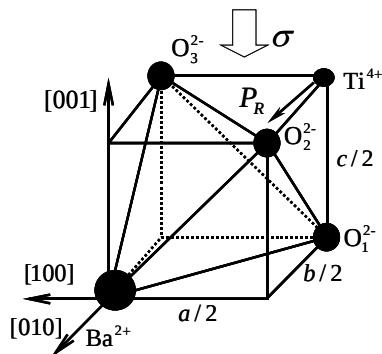


FIG. 3 THE CELL CALCULATION MODEL OF BaTiO₃ in R PHASE

In this paper, we calculate a single cell of BaTiO₃, the single cell should be the smallest periodic reduplicate cell, it includes one Ti⁴⁺ particle, three O²⁻ particles and one Ba²⁺ particle (Fig. 3). It is suggested that the initialized state of BaTiO₃ ferroelectric single crystal is R phase after {001} oriented polarization. Refer to literature[9], the crystal lattice constant of R phase BaTiO₃ ferroelectric single crystal is 4.001 Å, the coordinate of particle in single cell is shown in Table 1. The loading along {001} direction is carried out through application increasing strain by degrees. Stress and other parameters under each strain level is calculated by VASP. Calculation under each strain level include two steps. Firstly, the particle coordinate of single cell under each strain level is calculated by first principle molecular dynamic method. Secondly,

Stress and other parameters are obtained through relaxation that is based on the first result. Each increment of strain in this paper is 0.5%, until 4%.

TABLE 1 THE COORDINATE OF PARTICLE IN R PHASE BATIO3 FERROELECTRIC SINGLE CRYSTAL CELL

	100	010	001
Ba ²⁺	0	0	0
O ₁ ²⁻	0.5133	0.5133	0.0192
O ₂ ²⁻	0.5133	0.0192	0.5133
O ₃ ²⁻	0.0192	0.5133	0.5133
Ti ⁴⁺	0.489	0.489	0.489

Discussion

In order to validate that the method amentioned in this paper is correct, we calculate the elasticity constant C_{33} of T phase BaTiO₃ using the method mentioned before. Fig. 4 shows that the C_{33} is 180 GPa, which is approach to the experimental value 189 ± 8 GPa reported in refer[9]. This means that the method used in this paper is trusty.

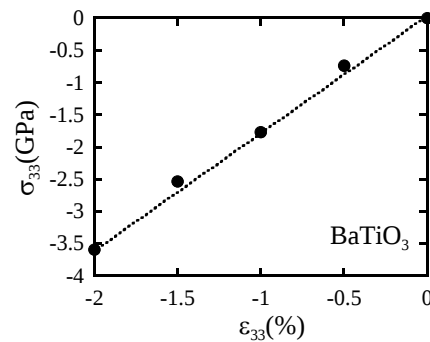
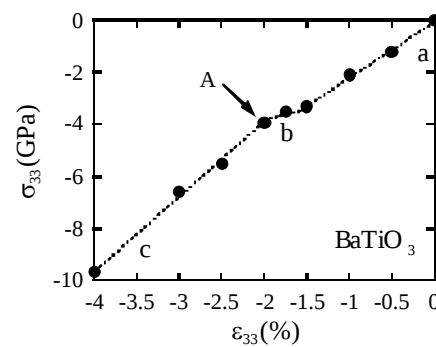


FIG. 4 THE STRESS-STRAIN CURVE OF BATIO3 FERROELECTRIC SINGLE CRYSTAL OBTAINED BY THE METHOD AMENTIONED IN THIS PAPER, THE {001} ORIENTED BATIO3 FERROELECTRIC SINGLE CRYSTAL IS IN T PHASE

Stress-strain curve of {001} orientated R phase BaTiO₃ calculated in first principle method is shown in Fig. 5(a). Fig. 5(a) shows that the result has similar nonlinear behavior to the experimental result of PMN-0.32PT during the loading that sketched in Fig. 2, namely, there is obvious “a,b,c” steps during loading.



(a)

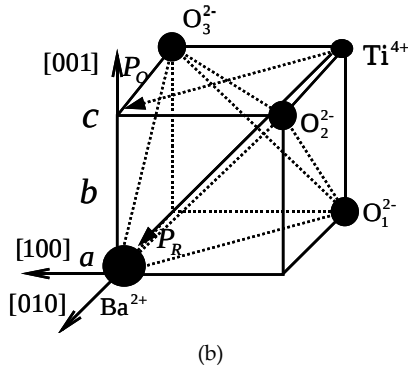


FIG.5(A)The STRESS-STRAIN CURVE of {001} ORIENTED BaTiO₃ FERROELECTRIC SINGLE CRYSTAL CALCULATED in FIRST PRINCIPLE CALCULATION, the SCATTER POINT is CALCULATION VALUE and the BROKEN LINE FIT the SCATTER POINT.(B) The SKETCH MAP of POLARIZATION ROTATION DURING the CALCULATION. The "A,B,C" LETTER in (B), the LETTER INDICATES DIFFERENT POLARIZATION STATES DURING LOADING.

The Viscoplastic Model of Ferroelectric Single

The Viscoplastic Model

From the experimental analysis, it is known that the <001>-oriented PMN-0.32PT single crystal undergo the $R \rightarrow M \rightarrow T$ and $R \rightarrow M \rightarrow O$ phase transformation under the compression. In order to establish a compact model and keep the essence of experiment, the R phase transformation of PMN-0.32PT is considered in this study. Polarization rotation cause bulk deformation and shear deformation associated with the slip planes. It is assumed that the corresponding deformation associated with the slip planes is shear dominated, a feature similar to that of the multi-slip system of the crystal plasticity. This similarity renders possible to use crystal plasticity models to describe the transformation deformation of PMN-0.32PT single crystal.

The poled ferroelectric single is four domain state, the polarization vector is along $\langle 111 \rangle, \langle \bar{1}11 \rangle, \langle 1\bar{1}1 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ respectively. In this study, it is assumed that the polarization vector of R phase can switch to the polarization vector of O phase, such as $\langle 111 \rangle$ vector switches to $\langle 001 \rangle$, the vector also can switch back from O phase to R phase. The polarization rotation has an analogy to crystal plasticity slip, so we suggest there is eight slip systems in PMN-0.32PT ferroelectric single crystal. According to the crystallographic theory, we suggest ferroelectric single crystal has possible 8 variants; transformation of variants can be characterized by the habit planes illustrated in Fig. 6. where n denotes the unit normal to the habit plane and s refers to the direction of transformation.

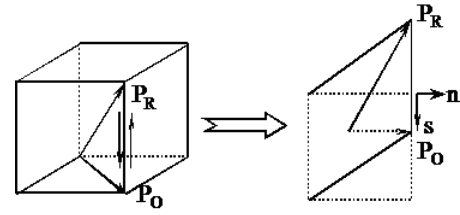


FIG.6 THE COMPARISON BETWEEN FERROELECTRIC PHASE TRANSFORMATION AND PLASTIC SLIP OF SINGLE CRYSTAL. N IS DIRECTION NORMAL TO SLIP SURFACE. S IS DIRECTION ALONG PHASE TRANSFORMATION.

In general, a criterion (i.e., the phase transformation criterion) exists for the phase transformation of ferroelectric single crystal, and the material is assumed to undergo phase transformation when at least one of the 8 variants satisfies the phase transformation criterion. This is detailed as follows. Upon loading, the condition to produce $R \rightarrow O$ polarization rotation on a specified habit plane is that the driving force G of that plane reaches the critical value G_{0O} . The driving force is composed of the chemical driving force G_{chem} and mechanical driving force G_{mech}

$$G = G_{chem} + G_{mech} = G_{0O} \quad (2)$$

A similar condition holds for reverse transformation from $O \rightarrow R$ polarization rotation with a critical value G_{0A}

$$G = G_{chem} + G_{mech} = G_{0A} \quad (3)$$

In Eqs. (2) and (3), the mechanical driving force can be expressed by

$$G_{mech}^r = \tau^a \gamma^* + E^a P^* \quad (4)$$

Where τ^a and E^a are the resolved stress on the "a" transformation system, and γ^* and P^* denote the associated transformation strain and transformation polarization. Following the crystal theory of plasticity, the resolved stress τ^a of the variant "a" is related to the stress tensor σ_{ij} and the Schmid factor α_{ij}^a by

$$\tau^a = \sum_{i,j=1}^3 \alpha_{ij}^a \sigma_{ij} \quad (5)$$

where the Schmid factor is defined as follow

$$\alpha_{ij}^a = \frac{1}{2} (m_i^a n_j^a + m_j^a n_i^a) \quad (6)$$

with m_i and n_i being the unit normal to the habit plane and shear direction to the variant "a", respectively. The resolved stress E^a of the variant "a" is related to the electrical field tensor E_i

$$E^a = \sum_{i=1}^3 E_i s_i \quad (7)$$

The chemical driving force in Eqs. (2) and (3) is assumed to be a linear function of the temperature

$$G_{chem} = \beta(T - T_0) \quad (8)$$

where T and T_0 denote the temperature in the single crystal and the equilibrium temperature respectively, and β is the stress-temperature coefficient. Note that the equilibrium temperature T_0 is defined as the average of the starting temperature of O phase transformation and that of R phase transformation, that is

$$T_0 = \frac{1}{2}(O_s + T_s) \quad (9)$$

When applying the rate independent crystal theory based model, Eqs. (2) and (3), to simulate the behavior of ferroelectric single crystals, one of the most computationally consuming tasks is to determine the set of instantaneously active transformation systems among the 8 possible variants at crystal level. This determination is usually achieved by an iterative procedure and must be carried out at each loading step, requiring extensive computation. Note that in the crystal theory of plasticity, a similar problem exists whilst in a rate dependent viscoplastic version of crystal theory of plasticity, determination of the set of active transformation systems is not necessary. As a result, computation effort can be reduced significantly. Following this idea, a viscoplastic version of Eqs. (10) and (11) are proposed and employed in this study. In the viscoplastic crystal model for PMN-0.32PT ferroelectric single crystals all transformation systems are assumed to be instantaneously active of varying extent, which is governed by a rate dependent viscoplastic law. In this paper, the phase transformation of variant "a" is assumed to comply with the following power law of viscoplasticity,

$$\dot{f}^a = \dot{f}_0 \left| \frac{G^a}{G_0} \right|^{\frac{1}{m-1}} \left| \frac{G^a}{G_0} \right| \frac{c}{c_0} \quad (10)$$

where $\dot{f}^a$ is phase fraction transformation rate of variant "a", $\dot{f}_0$ is reference phase fraction transformation rate, G^a is the driving force of variant "a", G_0 is the critical driving force, exponents k and m are material parameters dictating the rate effect, c depends upon the phase fraction, c_0 the reference value at initial state.

The phase fraction of variant "a" is calculated as,

$$\xi^a = f^a / f_0 \quad (11)$$

Summation over all possible variants provides the phase fraction for the whole ferroelectric single crystal, that is

$$\xi = \sum_{a=1}^8 \xi^a \quad (12)$$

The incremental form of Eq. (12) can be written as

$$d\xi^a = df^a / f_0 \quad (13)$$

The transformation strain tensor ε_{ij}^{tr} , which is associated with df^a , can be obtained as

$$d\varepsilon_{ij}^{tr} = \sum_{r=1}^8 \alpha_{ij}^a \gamma^* df^a \quad (14)$$

where α_{ij} is Schmid factor. $d\varepsilon_{ij}^{tr}$ is increment of phase strain. γ^* is the maximal strain transformation during loading. df^a is increment of phase fraction.

Elastic strain and electrical field induced strain during loading can expressed as

$$d\varepsilon_{ij}^e = C_{ijkl} d\sigma_{kl}, d\varepsilon_{ij}^E = d_{kij} dE_k \quad (15)$$

Increment of the total strain $d\varepsilon_{ij}$ can then expressed as the sum of an elastic component $d\varepsilon_{ij}^e$, a electrical field induced component $d\varepsilon_{ij}^E$ and a transformation induced component $d\varepsilon_{ij}^{tr}$,

$$d\varepsilon_{ij} = d\varepsilon_{ij}^e + d\varepsilon_{ij}^E + d\varepsilon_{ij}^{tr} \quad (16)$$

Numerical Results

To validate the model, the corresponding calculation result is compared to experimental stress-strain curve. The material parameters used in this study are as follow[10,11]. Material parameters of R phase are $C_{11}^R = 9.2\text{GPa}$, $C_{12}^R = 10.3\text{GPa}$, $C_{44}^R = 6.9\text{GPa}$, $\gamma^* = 0.0033$, $G_{0R} = 0.5073\text{MJ/m}^3$, $\beta = 0.004\text{MPa/K}$, $1/m = 11$, $1/k = 1.0$. $T = 403$, $T_0 = 298\text{K}$. Material parameters of O phase are $C_{11}^O = 38\text{GPa}$, $C_{12}^O = 40\text{GPa}$, $C_{44}^O = 28\text{GPa}$, $G_{0O} = 0.276\text{MJ/m}^3$, $\beta = 0.039\text{MPa/K}$, $1/m = 11.5$, $1/k = 1.1$. Fig. 12 shows the model predicted and experimental measured response. Result in Fig. 7 shows that stress-strain response of PMN-0.32PT can be predicted by the developed constitutive model, with quantitative agreement.

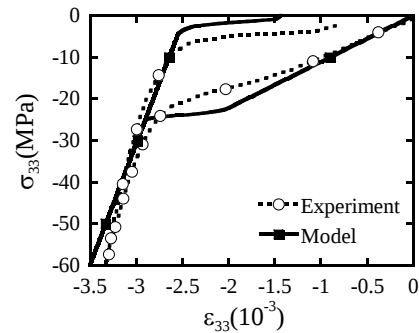


FIG.7 THE COMPARISON BETWEEN EXPERIMENTAL AND SIMULATION STRESS-STRAIN CURVE ALONG <001> DIRECTION OF FERROELECTRIC SINGLE CRYSTAL.

Conclusions

In this paper, polarization rotation model is developed to explain the observed behaviors of PMN-0.32PT. The stress-strain curves along $\langle 001 \rangle$ crystallographic direction of ferroelectric single crystal BaTiO_3 is calculated with the first principle method. Obtained results show that the $R \rightarrow M \rightarrow O$ polarization rotation takes place in BaTiO_3 ferroelectric single crystals under compression, which is consistent with the polarization rotation model. Based on the polarization rotation model, a constitutive model based on micro-mechanical model is proposed. It is shown that the developed model can faithfully capture the typical characteristic of the observed constitutive behavior of $\langle 001 \rangle$ -oriented PMN-0.32PT

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